Process-Directed Self-Assembly of Copolymer Materials

M. Müller

published in

NIC Symposium 2016
K. Binder, M. Müller, M. Kremer, A. Schnurpfeil (Editors)

Forschungszentrum Jülich GmbH,
John von Neumann Institute for Computing (NIC),
Schriften des Forschungszentrums Jülich, NIC Series, Vol. 48,
ISBN 978-3-95806-109-5, pp. 271.
http://hdl.handle.net/2128/9842

Process-Directed Self-Assembly of Copolymer Materials

Marcus Müller

Institute for Theoretical Physics, Georg-August University,
Friedrich-Hund-Platz 1, 37077 Göttingen, Germany
E-mail: mmueller@theorie.physik.uni-goettingen.de

Using computer simulations of a soft, coarse-grained particle model and numerical self-consistent field calculations, we study the kinetics of self-assembly of lamella-forming block copolymers. The role of non-equilibrium single-chain conformations, conserved densities and dependence of the complex free-energy landscape on the thermodynamic state are highlighted.

1 Introduction

Diblock copolymers are comprised of two, incompatible, flexible polymer blocks that are covalently bonded into linear amphiphilic molecules. The two blocks cannot macroscopically phase separate but, instead, self-assemble into spatially periodic structures whose length scale is dictated by the molecular extension, $R_{\mathrm{e}0}$. The equilibrium structure results from an interplay between the free-energy cost of internal AB interfaces and the entropy loss as the molecules stretch to uniformly fill space. Different morphologies are observed as a function of the volume fraction, f, of one of the blocks and the incompatibility, χN[1,2].

In experiments, however, the self-assembled structures often do not correspond to the thermodynamic equilibrium state but the kinetics of structure formation becomes trapped in a metastable state – e.g., the self-assembly without external guiding fields results in a finger-print like structure, and protracted annealing procedures using solvents or elevated temperature are required to improve long-range order[3]. Different metastable states can be categorised by their dimensionality: (a) metastable three-dimensional structures like the hexagonally perforated phase, (b) two-dimensional interfaces between grains of structures with the same symmetry but different orientations, or (c) localised defects like edge dislocations in a lamellar (smectic) structure or 5-7 defects in hexagonal structures[4].

Each of these structures corresponds to a local minimum of the free-energy landscape of the copolymer system, which has been likened to that of glass-forming systems[5]. In order to avoid defect formation or, alternatively, reproducibly direct the self-assembly into a specific metastable morphology, it is important to understand and control the kinetics of structure formation. To this end, one has to explore the complex, rugged free-energy landscape and devise process protocols that reproducibly steer the kinetics of self-assembly. Using two examples I discuss the following questions:

- What are the relevant slow collective variables that describe structure formation?
- What is the free-energy landscape as a functional of these slow variables and how to compute it?
- How can one control the evolution on the free-energy landscape?

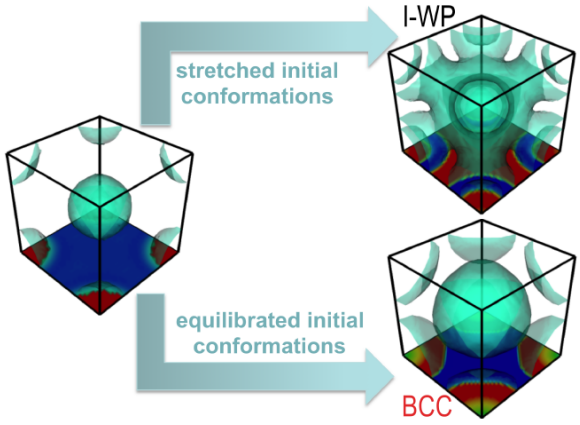

Figure 1. Illustration of the metastable morphologies obtained by kinetic Single-Chain-in-Mean-Field (SCMF) simulations of process-directed self-assembly by rapid expansion of a BCC morphology. The density-contour plots of the average morphology are obtained after back-folding the 27 unit cells of our large simulation box into a single unit cell. Adapted from Ref. 6.

2 Rapid-Quench Structure Formation

In the first example, we investigate the structure formation of a compressible AB block copolymer[6]. In the initial, high-pressure state, both segment types, A and B, are characterised by the same segmental volume and compressibility. The matrix component B is hardly compressible at all densities but the minority component exhibits a super-critical equation of state at lower densities. The fraction of A segments is $f = 1/4$, and a body-centred array of A-spheres is formed in equilibrium at high pressure. Then, the pressure is rapidly reduced, i.e., the system is affinely expanded in the computer simulation of our soft, coarse-grained particle model[7,8]. Right after the expansion, the density in the A-spheres and the B matrix is identical, but the pressure inside the A-spheres is much larger. Moreover the molecular conformations are stretched, in particular the long B block, which is comprised of the smaller segments. The system has two possibilities to establish mechanical equilibrium: (1) The pressurised A-spheres expand against the low-pressure B matrix, or (2) A segments can evaporate from the spherical A domains. The latter mechanism is facilitated by the tension in the B block that rips the short A fragments out of the A domain into the B matrix. In the simulations we observe that the A-spheres not only expand but that the density of A inside the matrix increases, this A excess in the matrix condenses and forms an additional bicontinuous A-rich network structure inside the B matrix. Thus a new, metastable morphology is formed: Schoen's I-WP phase[9] as illustrated in Fig. 1[6].

In order to assess, how important the stretching of the molecular conformations in the initial state is, we equilibrated the conformations in the expanded state at fixed density distribution by applying a field-theoretic umbrella potential[8]. This procedure corresponds to the basic assumption of self-consistent field theory, which asserts that the molecular conformations are in equilibrium with the instantaneous, non-equilibrium density distribution, i.e. the density is the only slow, collective variable. After removing the field-theoretic umbrella potential, the A-spheres only expand, but no additional A network in-

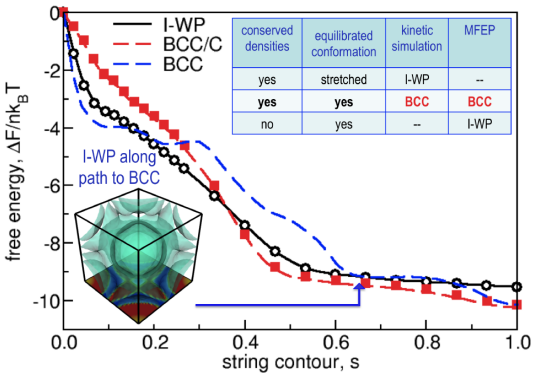

Figure 2. Minimum free-energy path (MFEP) from an expanded BCC morphology to an I-WP morphology or a BCC morphology ignoring the local conservation of the order parameter. Along the path to the BCC structure a metastable I-WP morphology forms at $s \approx 0.67$. Conserving locally the order-parameter, BCC/C, the MFEP directly passes from the BCC to the expanded BCC structure without additional metastable morphology along the path. The table summarises the finding of the SCMF simulation and MFEP calculations. Adapted from Ref. 6.

side the matrix is formed as shown in Fig. 1. Thus, these simulations demonstrate that non-equilibrium molecular conformations are important for the rapid, spinodal structure formation and can qualitatively alter the final structure. In principle, the importance of non-equilibrium molecular conformations must be generally expected because the time scale of spinodal structure formation, $\tau = {R_{e0}}^2/D$ (with D being the single-chain self-diffusion coefficient) is of the same order of magnitude as the Rouse time $\tau_R = \tau/3\pi^2$ that controls the relaxation of the molecular conformations in a non-entangled melt[10].

We also attempt to describe the structure formation by the minimum free-energy path of the free energy, $\mathcal{F}$, as a functional of the slow collective A density, $\phi_A(\mathbf{r})$, alone. The minimum free-energy path (MFEP)[11] is a sequence of structures, $\phi_A(\mathbf{r}, s)$, that depends on the continuous contour parameter $0 \leq s \leq 1$ and that is commonly defined by the condition that the thermodynamic force (i.e., gradient of the chemical potential) perpendicular to the MFEP vanishes, i.e., $\left(\frac{\delta \mathcal{F}}{\delta \phi_A(\mathbf{r},s)}\right)^{\perp} = 0$. Using large-scale computer simulations in conjunction with the improved string method[12], we have computed the MFEP from the affinely deformed BCC structure, and the results are presented in Fig. 2. We observe that the first minimum encountered is the I-WP structure even if we initialise the end-state of the string with the expanded BCC structure. This finding is in contrast to the dynamic SCMF simulation of the kinetics because the free-energy functional does not incorporate information about the non-equilibrium, stretched molecular conformations, and therefore should predict the expanded BCC structure as observed in the simulations with equilibrated chain conformations in the initial state.

This difference can be rationalised as follows: In the kinetic simulations we observed the I-WP structure because the stretched B-blocks pull A fragments into the matrix, whereas in the MFEP calculations the A density in the matrix increases along the path because the local conservation of density is not enforced and the evolution along the MFEP rather corresponds to Allen-Cahn instead of Cahn-Hilliard dynamics[13]. Instead, if we require that the composition current perpendicular to the path vanishes[14] – a requirement that

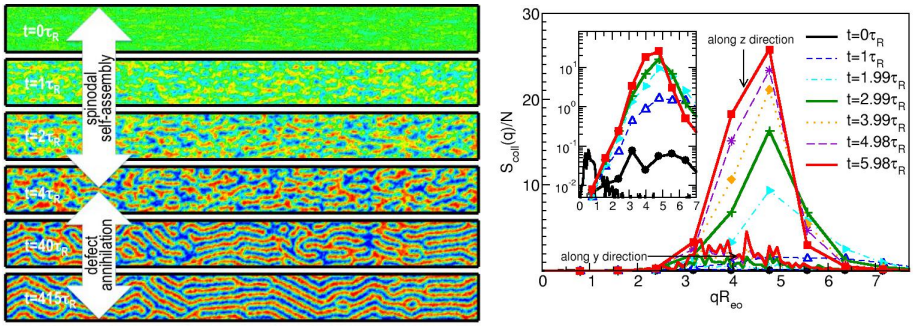

Figure 3. Left: Kinetics of structure formation after a quench of an uniaxial stretched disordered system, $\chi N = 0$, into the lamellar phase $\chi N = 20$. Top views of composition fluctuations are presented where the horizontal axis denotes the stretch direction and the vertical axis the undeformed one. Times, in units of the Rouse time $\tau_{\rm R}$, are indicated in the key. Right: Time evolution of the structure factor of composition fluctuations, $S_{\rm coll}(\mathbf{q})$, along the horizontal stretch directions, y, and perpendicular to it, z. The inset depicts the SCMF simulation data $S_{\rm coll}(q_z)$ on a log-scale to illustrate the exponential growth in the spinodal regime. $S_{\rm coll}(q_y, t = 0)$ is also shown as a line without symbols to demonstrate that the height of the peak of the structure factor in the initial anisotropic Gaussian state does not depend on the direction. Adapted from Ref. 22.

can be formally justified by including the Jacobian of the transformation from the particle coordinates, $\{\mathbf{r}\}$, to the collective density, $\phi_A(\mathbf{r})$[11,6,15] – the MFEP calculation BCC/C in Fig. 2 predicts the formation of an expanded BCC structure (in accord with the dynamic SCMF simulations).

3 Directing the Morphology by a Step-Like Elongation

The interplay between structure formation of the collective density, $\phi_A(\mathbf{r}, t)$, and the relaxation of the molecular conformation from a highly stretched, non-equilibrium state can be exploited to direct the large-scale orientation of the self-assembled morphology. This strategy is used in technical process like roll-casting[16–18] or melt-drawing[19] where experiments observe that the normals of the lamellar stripe structure are preferentially aligned perpendicular to the direction of an uniaxial stretch.

In our dynamic SCMF simulations we mimic this process by (1) equilibrating a polymer film in the disordered state, $\chi N = 0$, (2) affinely elongate the film by a factor $\lambda = 10$ along the horizontal y direction while compressing the film thickness so as to conserve the volume, and then (3) quench the system below the order-disorder transition, $\chi N = 20$. The last step corresponds to the evaporation of solvent after the step-wise elongation or the heating of the specimen above the glass transition temperature. The subsequent kinetics of structure formation is depicted in Fig. 3. During an initial spinodal regime, $t \leq 2\tau_{\rm R}$, composition fluctuations exponentially grow in time. We observe that they will increase much faster if the wavevector, $\mathbf{q}$, is aligned perpendicular to the stretch direction (lines with symbols) that in the parallel direction (lines without symbols). These spinodal fluctuations template the structure that, later, is merely improved by defect annihilation. In accord with experiment, we observe a preferential orientation of the lamella normals perpendicular to the stretch direction.

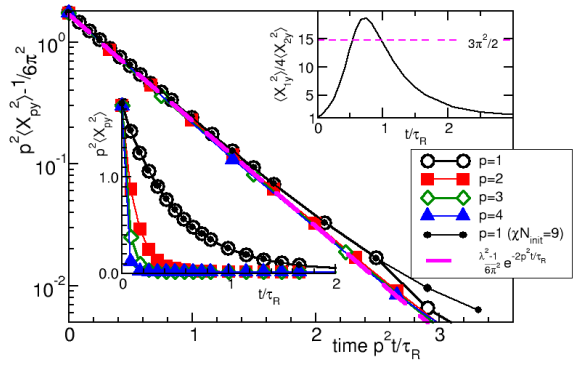

Figure 4. Time evolution of the variance of the first 4 Rouse modes $\langle X_{py}^2 \rangle$ along the stretch direction, y. The main panel presents the single-exponential relaxation with time scale $\tau_{\mathrm{R}}/2p^2$, whereas the left inset shows the unscaled data. The right inset depicts the time evolution of the ratio $\langle X_{1y}^2 \rangle / 4\langle X_{2y}^2 \rangle$, which adopts the value 1 for Gaussian chains. Adapted from Ref. 22.

At $t = 0$, the molecules are affinely deformed Gaussian chains with anisotropic statistical segment lengths in the different Cartesian directions. The anisotropy of the statistical segments is directly related to the anisotropy of the (single-chain) stress, $\Sigma_{\alpha\beta} = \frac{3k_{\mathrm{B}}T(N-1)}{V{R_{\mathrm{e0}}}^2} \sum_{\mathrm{bonds,i}} b_{i\alpha} b_{i\beta}$ where the Greek indices denote the Cartesian directions, x, y and z. If we use these anisotropic Gaussian chain conformations to compute the free energy of the lamellar phase within the self-consistent field theory or the structure factor of composition fluctuations, $S_{\mathrm{coll}}(\mathbf{q})$, according to the Random-Phase-Approximation[1], we will obtained the same result for the two directions – along the stretch direction, y, or perpendicular to it z – provided that we scale the length scale of the lamellar structure or the wavevector by the statistical segment length in that direction. Therefore, the thermodynamics of anisotropic Gaussian chain does not give rise to an orientational preference.

Whereas the initial, affinely deformed chain conformations and the final, equilibrated conformations obey (anisotropic) Gaussian statistics, the time evolution results in temporarily non-Gaussian conformations because the molecular structure on the large length scale retains the anisotropy longer whereas the small-scale structure quickly relaxes towards the isotropic state. During the spinodal stage, $t < 2\tau_{\mathrm{R}}$, the structure formation does not severely interfere with the conformational dynamics of the macromolecules because the bonded forces are significantly stronger than the non-bonded forces that give rise to structure formation. Thus, the conformational dynamics of our soft, coarse-grained particle model, which does not enforce the non-crossability of the chain molecules, obeys Rouse-like dynamics. Fig. 4 demonstrates that the individual Rouse modes exhibit a single-exponential relaxation behaviour during structure formation and that different modes, p, are characterised by the time scale, τ_{R}/p^2, like in a disordered melt. The non-Gaussianity of the molecular conformations can be quantified by the ratio of the first two Rouse modes, which is depicted in the inset of Fig. 4. We clearly observe strong deviations from the anisotropic Gauss behaviour during the spinodal time regime where composition fluctua-

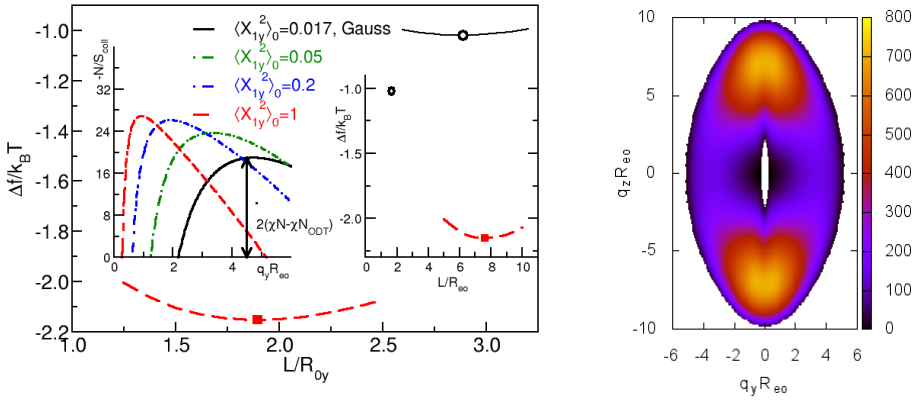

Figure 5. Left: Excess free energy per chain of the lamellar structure and negative, inverse structure factor in the disordered state at $\chi N = 20$ for non-Gaussian chains characterised by $\langle X_{1y}^2 \rangle = 1$. Right: Growth rate, $-\mathbf{q}^2/S_{\text{coll}}(\mathbf{q})$, of composition fluctuations in the disordered state at $\chi N = 20$. Adapted from Ref. 22.

tions exponentially grow, $t \approx \tau_{\text{R}}$.

Since the stress is comprised of all Rouse modes, however, it is not characterised by a simple, i.e., single-exponential relaxation behaviour. Moreover, if we restrained the diagonal components of the stress, the molecular conformations would remain anisotropic Gaussian[20,21]. Thus, it is more convenient to consider the variance of the slowest, first Rouse mode (instead of the virial stress), as slow collective variable that characterises the non-equilibrium molecular conformations.

In Fig. 5 (left) we study the thermodynamics of an ensemble of chains whose variance of the first Rouse mode along the stretch direction is fixed to $\langle X_{1y}^2 \rangle = 1$, whereas all other Rouse modes have relaxed to their equilibrium values. Since the Rouse mode is non-local along the chain, the conformations cannot be described by the Markovian propagator of self-consistent field theory, and we use a partial enumeration scheme with $n = 99\,840\,000$ single-chain conformations to compute the single-chain partition function or structure factor. Stretching or increasing $\langle X_{1y}^2 \rangle$ "polarises" the chains by increasing the distance between the centres of the A and B blocks. This effect gives rise to a thermodynamic preference of the ordering with lamella normals along the stretch direction. As shown in Fig. 5 (left), both the excess free energy per chain, Δf, as well as the thermodynamic driving force, $-1/S_{\text{coll}}(\mathbf{q})$, for composition fluctuations in the homogeneous disordered state suggest that lamella normals should be aligned along the stretch direction – in marked contrast to the result of the dynamic SCMF simulations and experiments.

Thus, we conclude that the orientation must be a kinetic effect[22]. Our SCMF simulations indicate that the orientation is decided during the regime of spinodal self-assembly. In Fig. 4 we demonstrated that the single-chain relaxation, which is governed by the strong bonded forces, is hardly affected by the spinodal structure formation. In turn, we expect that a spatially homogeneous deformation does not give rise to a current. Therefore the kinetics of ϕ_A is given by model-B dynamics[13] and we plot in Fig. 5 (right) the kinetic growth

rate of composition fluctuations, $-\mathbf{q}^2/S_{\rm coll}(\mathbf{q})$. Here the additional factor, q^2, arises from diffusive dynamics of the locally conserved composition. Indeed, Fig. 5 (right) reveals that the growth rate of fluctuations with $\mathbf{q}$ perpendicular to the stretch direction is significantly larger than for those with orientation y. Although these fluctuations are thermodynamically less favourable, their growth only requires transport over a shorter distance.

4 Concluding Remarks

The two examples – structure formation after a rapid pressure quench and after a step-wise elongation – illustrate that the structure formation of block copolymers is not only determined by thermodynamic equilibrium considerations of the density but that (1) the non-equilibrium molecular conformations during the early, spinodal stages of self-assembly and (2) the diffusive kinetics due to the local conservation of composition can qualitatively alter the predictions.

An appropriate theoretical description of these self-assembly processes from a highly non-equilibrium state cannot solely be based on the free-energy landscape as a functional of the collective composition but our simulations suggest that the variance of the first, slowest Rouse mode should be included as an additional variable. The qualitative properties of such a free-energy functional, $\mathcal{F}[\phi_A(\mathbf{r}), \mathbf{X}_1^2(\mathbf{r})]$ are largely unexplored. A complete description also has to complement the Cahn-Hilliard equation for the time evolution of the composition by a dynamic equation for the collective variable, $\mathbf{X}_1^2(\mathbf{r})$, that characterises the molecular conformations. In the present case, it simply followed Rouse dynamics of the disordered system but in general the coupling between conformations and morphology and also entanglement effects shall be considered. Such a theoretical framework will provide a general strategy to devise processes (e.g., temporal protocols for varying thermodynamic control parameters like temperature, pressure, mechanical strain or light-induced chemical transformations) that reproducibly direct the kinetics of self-assembly into long-lived metastable morphologies.

Acknowledgements

It is a great pleasure to thank De-Wen Sun and Jiuzhou Tang for enjoyable and fruitful collaboration. Financial support has been provided by the DFG Mu1674/14, SFB937 TP A04, and the EU-FP7 project CoLiSA.MMP. We gratefully acknowledge a generous grant of computing time at the John von Neumann Institute for Computing, Jülich, Germany.

References

1. L. Leibler, *Theory of microphase separation in block copolymers*, Macromolecules, **13**, 1602–1617, 1980.
2. F. S. Bates and G. H. Fredrickson, *Block Copolymers - Designer Soft Materials*, Physics Today, **52**, 32–38, 1999.
3. M. Müller and J. J. de Pablo, *Computational approaches for the dynamics of structure formation in self-assembling polymeric materials*, Annu. Rev. Mater. Sci., **43**, 1–34, 2013.

4. W. H. Li and M. Müller, *Defects in the self-assembly of block copolymers and their relevance for directed self-assembly*, Annu. Rev. Chem. Biomol. Eng., **6**, 187–216, 2015.
5. C.-Z. Zhang and Z.-G. Wang, *Random isotropic structures and possible glass transitions in diblock copolymer melts*, Phys. Rev. E, **73**, 031804, 2006.
6. M. Müller and D.-W. Sun, *Directing the self-assembly of block copolymers into a metastable complex network phase via a deep and rapid quench*, Phys. Rev. Lett., **111**, 267801, 2013.
7. K. C. Daoulas and M. Müller, *Single Chain in Mean Field simulations: Quasi-instantaneous field approximation and quantitative comparison with Monte Carlo simulations*, J. Chem. Phys., **125**, 184904, 2006.
8. M. Müller, *Studying amphiphilic self-assembly with soft coarse-grained models*, J. Stat. Phys., **145**, 967–1016, 2011.
9. A. H. Schoen, *Infinite periodic minimal surfaces without self-intersections*, NASA Technical Note TN D-5541i.
10. M. Doi and S. F. Edwards, *The Theory of Polymer Dynamics*, Oxford University Press, New York, 1994.
11. L. Maragliano, A. Fischer, E. Vanden-Eijnden, and G. Ciccotti, *String method in collective variables: Minimum free energy paths and isocommittor surfaces*, J. Chem. Phys., **125**, 024106, 2006.
12. W. E. W. Ren, and E. Vanden-Eijnden, *Simplified and improved string method for computing the minimum energy paths in barrier-crossing events*, J. Chem. Phys., **126**, 164103, 2007.
13. P. C. Hohenberg and B. I. Halperin, *Theory of dynamic critical phenomena*, Rev. Mod. Phys., **49**, 435–479, 1977.
14. W. Zhang, T. J. Li, and P. W. Zhang, *Numerical study for the nucleation of the one-dimensional stochastic Cahn-Hilliard dynamics*, Commun. Math. Sci., **10**, 1105–1132, 2012.
15. M. Müller and D. W. Sun, *Process-directed self-assembly of block copolymers: A computer simulation study*, J. Phys.: Condens Matter, **27**, 194101, 2015.
16. R. J. Albalak and E. L. Thomas, *Roll-casting of block copolymers and of block copolymer-homopolymer blends*, J. Polym. Sci. B: Polym. Phys., **32**, 341–350, 1994.
17. M. A. Villara, D. R. Rueda, F. Ania, and E. L. Thomas, *Study of oriented block copolymers films obtained by roll-casting*, Polymer, **43**, 5139–5145, 2002.
18. T. Xu, J. T. Goldbach, and T. P. Russell, *Sequential, orthogonal fields: A path to long-range, 3-D order in block copolymer thin films*, Macromolecules, **36**, 7296–7300, 2003.
19. T. Keller, C. Semmler, and K. D. Jandt, *Strain-induced phase morphology in melt drawn ultrathin highly oriented block copolymer films*, Macromol. Rapid Commun., **29**, 876–884, 2008.
20. G. H. Fredrickson, *Dynamics and rheology of inhomogeneous polymeric fluids: a complex Langevin approach*, J. Chem. Phys., **117**, 6810–6820, 2002.
21. T. Shima, H. Kuni, Y. Okabe, M. Doi, X. F. Yuan, and T. Kawakatsu, *Self-Consistent-Field Theory of viscoelastic behavior of inhomogeneous dense polymer systems*, Macromolecules, **36**, 9199–9204, 2003.
22. M. Müller and J. Tang, *Alignment of copolymer morphology by planar step elongation during spinodal self-assembly*, Phys. Rev. Lett., **115**, 228301, 2015.